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Plasmon enhanced luminescence of Tb/Eu co-doped film by Au NRs-PVA nanocomposite film

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1. The preparation of Au NRs

The seed solution was prepared firstly, 10 ml of 100 mM hexadecyltrimethyl ammonium bromide (CTAB) solution was mixed with 0.25 ml of 10 mM coloroarric acid (HAuCl₄) and stirred vigorously, 0.6 ml of 10 mM ice-cold NaBH₄ was added. The seed solution was stirred for 2 min and kept at 25 °C. Then the growth solution was prepared, 50 ml 100 mM CTAB solution was added to 0.2 ml 10 mM AgNO₃ solution. 2.5 ml 10 nM HAuCl₄ was added the solution. 0.3 ml 10 mM freshly prepared ascorbic acid solution was added. The final step was the adding of 12 μl seed solution and the mixed solution was gently mixed. The solution was followed to sit overnight to let the nanorods grow. The Au NRs were purified via centrifugation then resuspended in deionized water.

2. The comparison of the distribution of the pure Au NRs after drop-casting and the Au NRs in PVA film

The distribution of the pure Au NRs is shown in Figure S1. As shown in Figure S1a-b, the overall distribution of Au NRs throughout the substrate is characterized by the background scattering. The white light illumination is provided by a halogen lamp through an objective. The bright zones demonstrate the enhanced electric field distribution around Au NRs particles, hence the distribution of the bright zones demonstrate the dense region of Au NRs after drop-casting. For the pure Au NRs, the distribution demonstrate a series of rings, most of the Au NRs were concentrated on the ring, and there is little Au NRs for the area far away from the ring, which is known as the coffee ring effect[24]. As shown, the biggest ring is presented at the edge of the substrate. The SEM images near the rings are presented in Figure S1c-e, for the smaller ring as shown in Figure S1d, the Au NRs were single layer aggregated. For the bigger ring at the edge as shown in Figure S1e, the Au NRs were intensive.

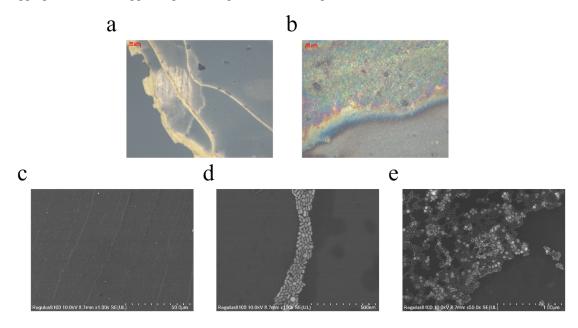


Figure S1. The distribution of the pure Au NRs: **a.** the microscope image of the small ring at the central zone. **b.** the microscope image of the ring at the edge of the substrate. **c-d.** The SEM image of the small ring at the central zone. **e.** The SEM image of the bigger ring near the edge of the substrate.

For the Au NRs-PVA film, it is hard to confirm the overall distribution of the Au NRs in PVA film by SEM/TEM images or the energy dispersive spectroscopy (EDS) mapping because the Au NRs are wrapped by PVA film. Due to the strong scattering of Au NRs, the bright spots would be observed with the increase of the amount of Au NRs. So, the scattering images can reflect the overall distribution of Au NRs to a certain extent. The corresponding microscope scattering images of Au NRs-PVA film from a central zone to the ring at the edge zone is shown in Figure S2a-d. As shown in Figure 2a, few bright spots can be observed at the central region of the substrate, which demonstrates the small amount of Au NRs. In the Figure S2b, there are some bright spots observed as the position moving from the central zone to the edge zone, which demonstrate the increase of the amount of Au NRs. For the zone near the edge shown in Figure S2c-d, there is a large amount of Au NRs, and the Au NRs agglomeration occurs at the edge zone.

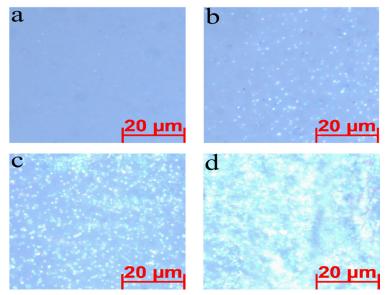


Figure S2. The microscope images of Au NRs-PVA film: a-d. From the central zone to the edge zone of substrate.

3. The EDS images of Au NRs-PVA film near the edge zone

The local distribution of the Au NRs near the edge is shown in Figure S3, which present the EDS mapping near the edge. As shown, the element of Au is found, however the distribution can not be accurately demonstrated because the Au NRs are wrapped by PVA film.

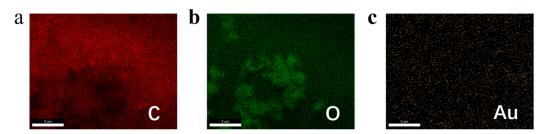


Figure S3. The EDS images of Au NRs-PVA film near the edge zone: **a.** The distribution of element C, **b.** the distribution of element Au.

4. The effect of the pure PVA and the Au NRs-PVA film on the luminescence

The luminescence of Eu was measured at 10 different longitudinal positions across the entire transverse range of the pure PVA film. The corresponding integrated intensity statistics is shown in Figure S4a. As shown, the photoluminescence is increased and then decreased again with the positions moving across the entire substrate. The luminescence based on the pure PVA film is slightly enhanced at the edge zone, and it has the greatest enhancement of about 2.5-fold at the central zone. The enhancement can be attributed to the enhanced adhesion of PVA surface compared with bare quartz substrates. For the sample with the Au NRs-PVA film, it is found that the photoluminescence is obviously improved, and the enhancement can reach several ten times. Here, the luminescence was measured at 40 different longitudinal positions across the entire transverse range of the Au NRs-PVA film due to the obviously variation of the luminescence intensity. The corresponding integrated intensity statistics is shown in Figure S4b. The greatest luminescence is obtained at the edge zone and then decreased gradually from the edge to the central zone. At the central zone, the integrated intensity still ranges rise and fall to some extent due to the few smaller rings. According to the distribution of Au NRs presented in Figure S2, the enhancement of the photoluminescence for the samples with Au NRs-PVA film is consistent with the distribution of Au NRs, which demonstrates that the Au NRs have a great effect on the photoluminescence enhancement.

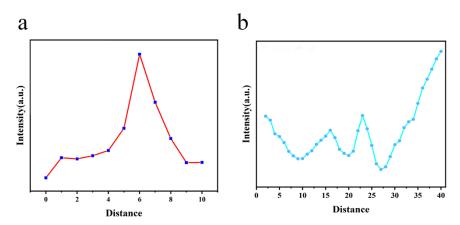


Figure S4. The integrated luminescence intensity statistics of Eu/Tb film across the substrates of the pure PVA film and the Au NRs-PVA film. **a.** the pure PVA film **b.** the Au NRs-PVA film.

5. The comparison of enhancement factor under excitation of 292 nm and 360 nm

The comparison of the enhancement factor under excitation of 292 nm and 360 nm is shown in Supplementary Figure S5. The enhancement of 612 nm under excitation of 360 nm is maximum, the maximum can reach to 71.5-fold. Under excitation of 292 nm, although the samples are excited under the characteristic excitation of Tb, the enhancement factor at the emission of 612 nm is greater than that at the emission of 545 nm.

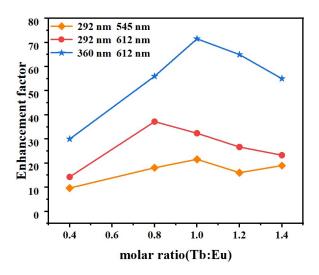


Figure S5. The comparison of the enhancement factor under excitation of 292 nm and 360 nm.